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EVALUATION OF PORCELAIN WHITENESS

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The particulars of the application of the colorimetric method for evaluating the whiteness and yellowness of porcelain are examined. The whiteness index of porcelain makes it possible to rank samples according to preference, which is the basis for evaluating their competitiveness and for sorting articles during production. Samples of solid porcelain cannot be distinguished from bone porcelain solely according to the whiteness or yellowness index, but it can be done in CIE $L^*A^*B^*$ colorimetric space coordinates.

Whiteness is the most important quality characteristic of porcelain articles which determines their competitiveness. At the present time, the whiteness of porcelain articles is determined according to be GOST 24768–2000 method in the form of an integral spectrophotometric index, based on measurements of the spectral reflection coefficients for the wavelengths 400, 540, and 700 nm. In accordance with a draft of the federal law (special technical regulation) “On the safety of ceramic dishware” the “whiteness” index will be a mandatory index for porcelain identification [1]. However, there are a number of limitations on the use of this method for measuring whiteness for this problem.

In the first place, the spectrophotometric method used in the standard indicated above for measuring the whiteness of porcelain is basically intended for measuring the quality of material according to the whiteness and makes it possible, at least, to solve the problem of sorting porcelain articles. In our view, monitoring quality according to whiteness should not be equated, as is often done, with a colorimetric evaluation of white material. In principle, a method of instrumental monitoring of whiteness for sorting product and a method of colorimetric evaluation, making it possible to identify ceramic materials according to color indices and measure color differences between a finished product and a control sample, should be developed.

In the second place, the standard method described above for measuring whiteness does not harmonize with other international normative documents and, consequently, is not used in international practice for specifying the white color of materials.

In this connection, a topical problem is choosing a method of colorimetric evaluation of the color of white porce-

lain and a system of indices for distinguishing the color of porcelain according to the type of material. It is known that an expert can distinguish by visual assessment samples of solid porcelain from bone china samples quite accurately. Therefore, it is possible to find a system of indices for distinguishing color.

Whiteness can be characterized by a property of a scattering surface which indicates its color similarity to a certain standard white color or preferred white color [2]. Whiteness is a subjectively perceived property. Color is a phenomenon, arising as a result of the interaction of photons, the object, and the observer. These three factors together are called a “visual situation” and give rise to color perception.

The perception of whiteness depends not only on the overall quality of reflected light but also on its spectral composition. Consequently, it is obvious that whiteness evaluation must take account of the color characteristics of a sample and be based on color measurements.

The color white is a name, and it occupies a small region of color space, has high lightness and low saturation simultaneously, and is distinguished according to the color tone.

The international commission on illumination (MKO, or in international terminology CIE) determines the lightness for which the approximate correlator is L^* as the perceived brightness for evaluating whether a surface emits more or less light on the basis of the ratio to the perceived brightness of the white surface of a standard sample.

The term “perception of chromaticity” (chromaticness) serves to describe whether the perceived color of a surface is more or less chromatic. Saturation is a property of visual perception, which makes it possible to judge the amount of chromatic color irrespective of the amount of a chromatic color, and the color tone is a sensation denoted by symbols: blue, green, color, and so on.

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As a rule, several terms are used to determine whiteness. Aside from the term whiteness, which is a general term, the concept brightness is also used. The latter is related only with whiteness obtained by performing measurements at a single wavelength ($\lambda = 457$ nm), i.e., it is necessary to determine the index of reflection in the blue region of the spectrum (the coefficient R_{457} is essentially equivalent to the color coordinate Z of the XYZ CIE 1931 colorimetric system). For ceramic materials with a yellow tinge, the yellowness parameter (yellow hue, degree of yellowness) is used together with the concept of whiteness.

In contrast to most well-known indices of properties whose values are expressed in terms of a single number (meter, degree, second, and so on), the result of evaluating, including white, is a set of three numbers, i.e., color is a three-dimensional quantity. In addition, aside from the properties of the object itself, the properties of our vision and the character of illumination are also taken into account. Consequently, the evaluation of the whiteness of porcelain by using a one-dimensional scale as a combination of the magnitudes of opposing processes of color perception (black-white, red-green, and blue-yellow) does not always explain the discrepancy in the color of samples of porcelain articles which have the same whiteness values. The difficulty of constructing a metric scale for evaluating the whiteness of porcelain is due to the interrelation of two phenomena of color perception. The first one is the ratio of lightness and chromaticity (characteristics of the object) and the second is color preference (a characteristic of the subject, for example, “preferred white”) which is determined, in turn, by a strict comparison of the concepts “object – color,” “color memory,” and so on.

Porcelain samples which gave different color perceptions when compared in pairs could turn out to be white. If two white samples differ only according to lightness, then the lighter sample is perceived as being whiter. If one of the samples is lighter but possesses less blueness and more yellowness, then depending on the balance of lightness and blueness, it will be perceived as whiter than the other sample or vice versa [3].

For example, bone china possesses simultaneously large values of the lightness ($L^* > 92$) and yellowness (B^* — from 2.5 to 5) as opposed to high-feldspar (soft) porcelain, which possesses high lightness but low yellowness ($L^* \sim 90$, $B^* < 1.5$). Experts comparing objects in pairs prefer bone china.

In this connection, there exists the concept “preferred white color” and different materials occupy a different region of the color space [2]. When choosing a standard for the color white (“customary – not customary”) for different materials, the question is solved on the basis of experimental data with the help of experts [4]. When experts choose a standard on the basis of an emotional assessment, it is not the sensorial space that is actualized with respect to accuracy and subtleness of distinction but rather the value of the color for the subject, i.e., the space of judgments about color, indi-

vidual taste, and experience. For the subject, evidently, color is that which is extracted from memory plus the value of the object.

All this could mean that a unique relation between the perceived whiteness of a material and the colorimetric characteristics, evidently, does not exist.

Whiteness as any other form of perception cannot be measured. Only the physical quantities that give rise to the senses can be measured. In the case at hand, one or another property of the energy of radiation is measured to evaluate whiteness.

Instrumental methods for evaluating the whiteness of materials are divided into spectrophotometric and colorimetric, taking account of the fact that to evaluate whiteness a measurement is made according to one or another method — the spectral coefficients of reflection of the material or the colorimetric characteristics of the material. At the present time, CIE recommends the colorimetric method [3]. The instrument which is ordinarily used to evaluate color is called a spectrophotometer.

No two models of spectrophotometers show the same measurement result for the same sample. This is due to differences in the construction of the instruments, the area of a sphere, the size and position of openings in the sources of color, and so forth. Properties of a sample such as texture, finish, luster, and luminescence can increase the differences [2, 3]. For this reason, it is correct to compare the spectral colorimetric characteristics of porcelain samples obtained on the same spectrophotometer.

Basic Standards in Colorimetry. Color measurements must be performed under identical conditions. Otherwise the results cannot be compared. Three conditions affect the result of color measurements [2]:

- geometry of illumination, observation;
- source of illumination;
- standard colorimetric observer.

The perceived color depends to a large extent on how the sample is illuminated and observed, i.e., on the methods and angles of illumination/observation.

CIE has recommended different geometries for optical measurements which reduce to two main geometries: $d/0$ and $45/0$. The geometry $d/0$ or $d/8$ using a sphere is provided in instruments whose main problem is to measure color (preferable for calculating prescriptions). The light scattered from the inner surface of a sphere eliminates a sample uniformly, which reduces the influence of the surface finish of a sample to a minimum. Such instruments are equipped with a mirror trap and are arranged so that the light reflected from the sphere, being reflected orthogonally from surface of the sample, cannot reach the photodetector. The $45/0$ geometry always results in exclusion of the specular component and its design is close to the one used in a camera for evaluating color. In this connection, there is a tendency to use this geometry when quality is being monitored. However, because of the radiation is directed at an angle of 45°

with respect to the sample the result depends more on the structure (finish) of the surface — when the sample is rotated, the spectral reflection curve will change and the color coordinates will change correspondingly.

At the present time, CIE recommends that color characteristics be measured for two “standard colorimetric observers:” the 1931 CIE observer with a 2° field of view, which corresponds to the size of the yellow spot of the eye sheath, and the 1964 CIE observer with a 10° field of view, which is considered to be more appropriate for performing investigations by visual balancing of colors.

CIE recommends different artificial sources of light as standard radiation for monitoring the color of materials. The most widely used sources are standard sources A , C , and D_{65} : A) corresponds to a standard incandescent lamp, C) corresponds to northern daylight, and D_{65} is close to the source C but with a more natural content of ultraviolet light [2, 3]. The illumination/observer conditions are taken to be conventionally $C/2^\circ$ or, more often in recent years, $D_{65}/10^\circ$.

There exist many sources of light, including incandescent and luminescent lamps which can be used to observe an object; the most important source is daylight. Different phases of daylight are distinguished, such as light from a blue sky, direct sunlight, and the light from a cloudy sky. Experience shows that if the manufacturer is interested in a definite color for an article under daylight illumination, then there is no need to monitor the color for all phases of daylight. The need to evaluate color for different sources of light arises when the article and the standard have the same color under the same illumination and different colors when a different source of light is used. For example, such color distinction is possible for porcelain or glass colored with definite pigments [5].

The normal human eye can distinguish from 7 to 10 million colors. In this connection, different methods have been developed to organize information about color. There are several mathematical systems which identify color using coordinates that can describe any color. Different systems of color space have been developed. Two such systems — XYZ CIE 1931 and $CIE L^*A^*B^*$ 1976 — are widely used in industry and science [2–4]. The color coordinates X , Y , and Z say nothing about the color of a sample, although with experience we can imagine color quite well according to its values. These quantities were intended not for practical description of the color of objects but rather to determine whether or not colors with the same coordinate values (with the standard illumination and observer) are actually the same. As a result, color coordinates are often transformed into a more understandable system of coordinates (x, y, Y) which often are represented as a diagram, called the CIE 1931 color space.

The system of chromaticity coordinates x, y and the color coordinate Y , associated to brightness (lightness) of an object, is ordinarily a formal specification of a color. All colors can be encompassed by examining the values of Y and the coordinates x, y drawn on a colorimaticity plot. A line con-

necting spectral colors is known as the spectral chromaticity curve. Aside from the chromaticity coordinates, the plot makes it possible to determine the dominant (or additional) wavelength and the conventional frequency of a color. Such a system is very convenient for evaluating the color of ceramic and glass articles [5], but it is ineffective for evaluating the whiteness of porcelain.

Another popular method for evaluating the color of porcelain samples is based on the use of iso-contrast indices of the colorimetric system $CIE L^*A^*B^*$ 1976 [2, 3].

Analysis of the relationship between the values of the porcelain indices in the colorimetric system $CIE L^*A^*B^*$ 1976 with indices of the microstructure, chemical composition, and parameters of the firing regime made it possible not only to develop technological techniques for increasing whiteness [6–8], but also to explain the nature of the color and the mechanism for coloring porcelain [9, 10].

Whiteness. After many international investigations organized by CIE and for purposes of uniformity, CIE adopted a whiteness relation in the form of the equation

$$W_{ISO} = Y + 800(x_n - x) + 1700(y_n - y),$$

where Y is the color coordinate associated with brightness (likeness); x, y are the chromaticity coordinates of the sample; x_n and y_n are the chromaticity coordinates of the achromatic point for the chosen CIE 1931 observer (2 and 10°).

The larger the value of W_{ISO} , the whiter the sample is. The equation indicates that the whiteness W_{ISO} is determined by the brightness Y and the index $800(x_n - x) + 1700(y_n - y)$, which increases the whiteness as the color of the material shifts toward blue and decreases the whiteness as the color becomes more yellow. In 1987 the CIE whiteness relation was included in the standard ISO 105-J02.

Yellowness. The most common color hue of white porcelain is yellowness. Different relations have been developed for evaluating yellowness using instruments, though not as many relations as for evaluating whiteness. The perception of yellowness is caused by the fact that the absorption of the blue region of the spectrum is much greater than absorption in other regions of the spectrum. Many whiteness relations are normalized to low absorption of the sample in this region by including the characteristic $(cZ - X)$ or $(cZ - Y)$, where c is a constant and X, Y, Z are the CIE 1931 color coordinates.

The most commonly used method is described in the standard ASTM D 1925–70 [2, 3]. The yellowness index G was specially developed to determine the degree of yellowness of uniform non-fluorescent materials whose color is close to white. According to ASTM D 1925 the yellowness index G is calculated according to the following relation:

$$G = [(1.28X - 1.06Z)/Y] \times 100,$$

where X, Y, Z are the color coordinates of a sample in the CIE 1931 system.

TABLE 1.

Sample	Manufacturer of the porcelain sample	Measurement regime*	L^*	A^*	B^*	H^*	$G, \%$	W_{ISO}
1	Wtactawek, Poland	I	86.37	-0.96	1.30	126.37	2.21	62.24
		II	89.58	-1.17	0.60	152.65	0.56	72.50
2	Royal Crown, Porcelain of England	I	86.38	-1.18	0.42	160.54	0.16	66.70
		II	89.68	-1.26	-0.46	200.02	-1.71	77.86
3	Dulevo	I	83.76	-1.17	2.50	115.12	4.63	50.80
		II	86.86	-1.23	1.94	122.32	3.30	60.10
4	Studio Ten, made in Sri Lanka	I	86.39	-1.31	0.53	157.90	0.29	66.14
		II	87.43	-1.43	0.85	149.10	0.87	66.70
5	Royal Crown, Porcelain of England	I	89.49	-1.74	0.32	169.70	0.50	73.72
		II	89.96	-1.78	0.97	151.50	0.80	71.56
6	Original Bohemia	I	85.71	-1.49	0.76	153.10	0.62	63.63
		II	86.95	-1.77	1.31	143.50	1.53	63.43

* I) without the specular component of the reflected light flux, II) with the specular component of the reflected light flux.

According to this relation, the higher the value of G , the more yellow the porcelain is; for $G \sim 0$ there is no yellow hue; and, for $G < 0$ the material has a blue hue.

Standard CIE-recommended methods are used for the colorimetric evaluation of porcelain. Ninety-four samples of porcelain articles in the form of dishes and small plates with an even, smooth surface greater than 200 mm in size, differing with respect to the type of porcelain (hard or bone) and country of origin (Russia, Japan, Germany, Czechoslovakia, China, and others) were chosen as the objects.

The color of the samples was measured on a Pul'sar spectrophotometer with optical measurement geometry $d/8$ with radiator C and CIE 1931 observer position equal to 2° , neglecting and taking account of the specular component.

Table 1 gives the coordinates of porcelain samples in the system CIE $L^*A^*B^*$ as well as the values of their whiteness W_{ISO} and yellowness G based on measurements of the reflection spectrum taking account of and neglecting the specular component.

For all porcelain samples, when the reflection spectrum is measured taking account of the specular component as opposed to the corresponding values neglecting the specular component, it is characteristic that, in the first place, the values along the lightness coordinate L^* increase (ΔL^* from 0.5 to 3.0) and, in the second place, the chromaticity coordinates change from one sample to another in different directions: the yellowness coordinate B^* decreases negligibly for samples 1–3 and increases for samples 4–6.

In contrast to many white materials (paper, fabric, and so forth), the character of the light scattering by glazed porcelain is mixed, i.e., both the specular and diffuse components are present in the reflected light. Consequently, samples with the same color and the same degree of brightness in all directions of observation will be evaluated as being identical. At the same time, samples with different degree of brightness

but chromatically identical can have the same color perception only under certain conditions of measurement. They are goniometrically metameric.

Specular reflection is described by Fresnel's equation [2] and theoretically comprises, on average for glazed porcelain, no more than 4%. The smoother the surface of the glaze, the greater its specular component is. In reality, a glazed porcelain surface consists of many very small sites whose slopes are different. The roughness of the surface can be conventionally divided into two components: micro-roughness of the same or smaller size than the wavelength of the light and giving rise to diffraction of light; macroroughness, which changes the angle of the specular reflection.

A visual evaluation of the whiteness of porcelain with high luster will show greater whiteness than for samples with a similar composition but lower luster. This is explained by the fact that the specular reflection is a surface phenomenon, so that the reflected light does not interact with the coloring impurities in porcelain. The specular reflection is colorless, i.e., the reflected light has the same spectrum as the light source, so that visually such a material appears to be whiter.

Since the whiteness W_{ISO} is a function of the lightness and chromaticity coordinates, its values either increase (samples 1–3) or decrease (sample 5) or remain essentially constant. Since for reflection from porcelain the specular component depends mainly on the state of the surface of the glaze, which is determined by many factors, it is best to neglect the specular component when evaluating the color of porcelain.

The color coordinates of porcelain lie in a compact region of the CIE $L^*A^*B^*$ colorimetric space in the form of an ellipsoid elongated along the coordinate L^* predominantly in the yellow (B^*)–green (A^*) zone of chromaticity: L^* —from 76 to 96, B^* —from 0 to 7 (see Fig. 1).

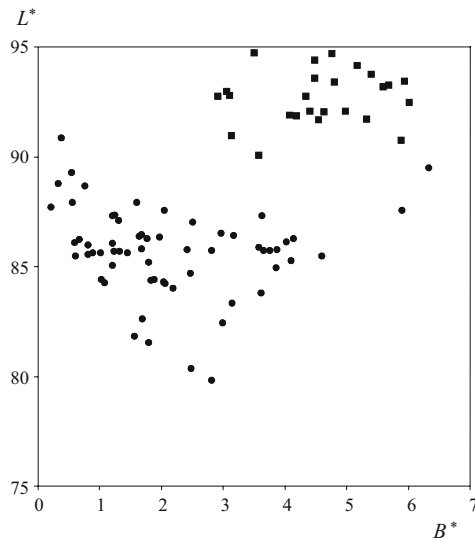


Fig. 1. Arrangement of the values of the color coordinates of porcelain samples (lightness L^* and yellowness B^*) in the plane of the CIE $L^*A^*B^*$ colorimetric space: ●, ■) solid porcelain and bone china, respectively.

Table 2 gives the color coordinates L^* , A^* , B^* , the values of the color hue H^* , yellowness G , and whiteness W_{ISO} of samples of solid porcelain, and Table 3 gives the values for

bone china. As one can see, the whiteness of solid and bone porcelain (from 41 to 76 and from 60 to 69%, respectively) and the yellowness (from 0.1 to 11.3 and from 5.8 to 7.0, respectively) considered separately cannot be used as indices to distinguish the color of porcelain according to the type of material. Although, samples of solid and bone porcelain can be easily distinguished as being of two types in the coordinate plane $L^* - B^*$ (lightness – yellowness); see Fig. 1.

Now it is necessary to determine, in the first place, the porcelain region in the colorimetric coordinate system of the CIE $L^*A^*B^*$ and, in the second place, the zone of this region corresponding to “preferred whiteness.”

According to Table 2, the increase of the whiteness of porcelain samples is due to, first and foremost, a decrease of the yellowness coordinate B^* , which, in turn, shifts the color type from the yellow axis ($H^* = 90$) to the green ($H^* = 180$) axis: from $H^* = 101.4$ (Narumi sample) to $H^* = 162$ (SiuFung sample). In this case the fraction of reflection in the yellow part of the spectrum decreases and that in the green part of the visible spectrum increases. Experimental investigations of the perception of objects with different fractions of monochromatic light in the reflection spectrum confirm [3] that for negative values along the coordinate A^* (green) perception of yellowness decreases, and for positive values of A^* (red) the perception of yellowness increases.

TABLE 2.

Manufacturer of porcelain sample	L^*	A^*	B^*	H^*	G , %	W_{ISO}
SiuFung	90.87	− 1.18	0.38	162.39	0.08	76.42
Royal Crown	89.28	− 1.81	0.55	162.98	0.07	72.11
Yokko Hissan	87.34	− 1.76	1.25	144.68	1.41	64.56
Studio Ten	86.23	− 1.40	0.67	154.43	0.51	65.14
Wtoctawek, Poland	86.37	− 0.96	1.30	126.37	2.21	62.24
Lubiana, Poland	87.93	− 1.46	1.61	132.30	2.41	62.67
BKW, Fine Royal Porcelain	88.65	− 1.94	0.77	158.41	0.26	69.70
Karolina, Studio Collection	86.32	− 1.43	1.97	126.01	3.21	58.78
LFZ	85.71	− 1.20	2.82	112.95	5.23	56.92
MZ, Czech Republic	84.22	− 1.39	2.07	123.91	3.51	53.93
LFZ	86.51	− 0.18	2.97	111.74	5.48	50.04
Verbilki	85.27	− 1.49	4.10	110.00	7.65	47.81
Kuban'farfor	83.32	− 0.65	3.14	101.63	6.48	46.55
Narumi	87.54	− 1.19	5.90	101.40	11.29	41.84

TABLE 3.

Manufacturer of porcelain sample	L^*	A^*	B^*	H^*	G , %	W_{ISO}
LFZ	91.88	− 1.61	4.08	111.48	7.04	60.52
Villeroy & Boch	94.69	− 2.58	4.77	118.40	6.58	68.70
Duchess, Fine bone China	94.40	− 1.94	4.49	113.40	7.42	63.40
NIKKO company, Fine Bone China	92.74	− 0.29	2.92	95.74	5.81	68.62
Royal Albert, Bone China	94.74	− 1.31	3.51	110.50	6.02	69.28

For solid porcelain, the brightness values $W_{\text{ISO}} > 60\%$ are possible with lightness values $L^* > 86$ and yellowness values $B^* < 2$; for bone porcelain — $L^* > 91$, B^* — from 2 to 4.5

In summary, it is impossible to distinguish samples of solid porcelain from bone porcelain according to a single whiteness index only. The whiteness of porcelain makes it possible to rank samples according to preference, which is the basis for evaluating their competitiveness and for sorting articles during production.

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